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NOTE

Effect of Number of Coherent Lamellae on Small-Angle Scattering

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Intensity function of small-angle scattering for one-dimensional lattice of regularly stacked lamellae is derived as a function of degree of crystallinity $\alpha=D/L$ (D : lamellar thickness, L : long spacing) from the general function of Wenig and Brämer. Using this reduced function, the effect of size of lamellar cluster or number of coherent lamellae on small-angle scattering is examined, and 25% of the difference between long spacings of bulk polyethylene calculated from the first and second order reflections has been elucidated by assuming the initial number of lamellae in the cluster to be six.

KEY WORDS: Small-angle scattering/ One-dimensional lattice model/ Size effect of lamellar cluster/ Degree of crystallinity/

INTRODUCTION

Reinhold, Fischer, and Peterlin[1] tried to explain the difference between long spacings calculated from the first and second order reflections in the small-angle X-ray scattering of bulk polyethylene using a concept of distance fluctuation in stacked lamellae. Tsvankin[2] and Crist[3] also discussed such a problem on this line. However, recent electron microscopic studies show that the number of coherently stacked lamellae in undrawn samples is not so large ; Tagawa *et al.*[4,5] found superlamellar structure in blown polyethylene films by high resolution scanning electron microscopy, each superlamella consisting of five to ten lamellae. Kanig[6,7] also observed a lamellar cluster structure in bulk crystallized polyethylene samples though he did not clearly describe this. When the number of coherent lamellae is very small, *e.g.*, less than eight, the effect of size of superlamella on small-angle scattering cannot be neglected as well as that of the distance fluctuation in the lamellar cluster. In this note, therefore, the effect of the number of coherent lamellae on the small-angle scattering is investigated.

THEORY

One-dimensional lattice consisting of coherently stacked lmellae is considered in this study. The general intensity function for this model was first derived by Hosemann,[8] and then modified by Wenig and Brämer.[9] In the case of no distance fluctuation within the cluster, this intensity function is reduced to

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$$I(\xi)=L^2(\rho_c-\rho_a)^2\left[\frac{\sin(\pi N\xi)}{\pi\xi}\right]^2\left\{\left[\frac{\sin(\pi\alpha\xi)}{\sin(\pi\xi)}\right]^2-2\alpha\frac{\sin(\pi\alpha\xi)}{\sin(\pi\xi)}\cos[\pi(1-\alpha)\xi]+\alpha^2\right\}. \quad (1)$$

Here, $\xi(\neq 0)$ is the reciprocal lattice coordinate, $\alpha=D/L$ is the degree of crystallinity in volume fraction, D and L are lamellar thickness and long spacing, respectively, N is the number of coherent lamellae in the cluster, and ρ_c and ρ_a are the densities in the crystalline and amorphous regions, respectively. In eq. (1) the average density $\bar{\rho}$ of a given sample is assumed to be

$$\bar{\rho}=\alpha\rho_c+(1-\alpha)\rho_a. \quad (2)$$

The first term in the braces of eq. (1) represents the structure factor within the cluster and the others are correction terms when these clusters are densely packed in the sample ; it should be taken into account that the clusters are not in vacuo but in the average density of the sample. When $\alpha=0$ or 1, $I(\xi)=0$, which confirms the validity of eq. (1). The eq. (1) gives the intensity function for the nth order reflection as

$$I(n)=L^2(\rho_c-\rho_a)^2(N/n\pi)^2\sin^2(n\pi\alpha). \quad (3)$$

Figure 1 shows the change of intensity as a function of degree of crystallinity for various orders of reflection. In the case of the first order reflection, the intensity has a maximum when $\alpha=0.5$, whereas that of the second order reflection has two maxima at $\alpha=0.25$ and 0.75 and is zero at $\alpha=0.5$. Generally, the intensity function of the nth order reflection gives n maxima at $\alpha=1/2n$, $3/2n,\ldots$, and $(2n-1)/2n$, and is zero at $\alpha=0$, $1/n$, $2/n,\ldots$, and n/n. All of the intensity curves in Fig. 1 are symmetric at $\alpha=0.5$, as is presumed from Babinet's theorem.

The peak positions of the first and second order reflections calculated from eq. (1)

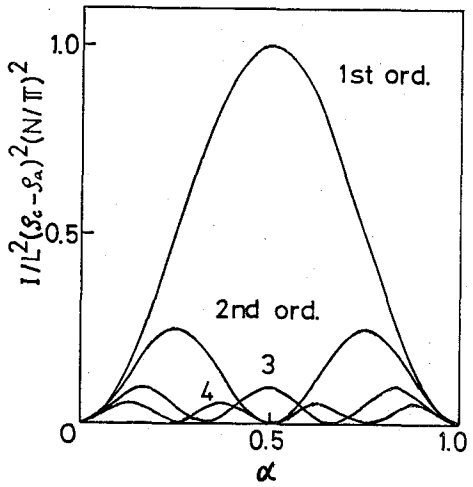

Fig. 1 Peak intensity for various orders of reflection as a function of degree of crystallinity, α.

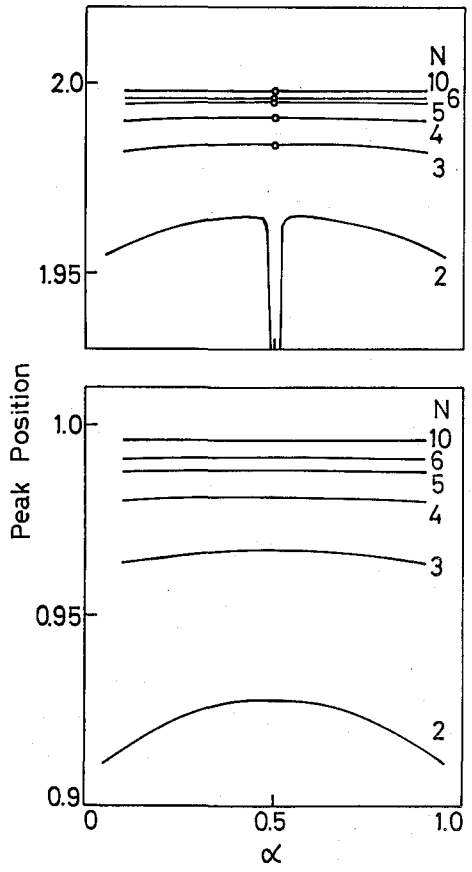

Fig. 2 Peak position versus degree of crystallinity α for the first and second order reflections. N is the number of coherent lamellae in a superlattice.

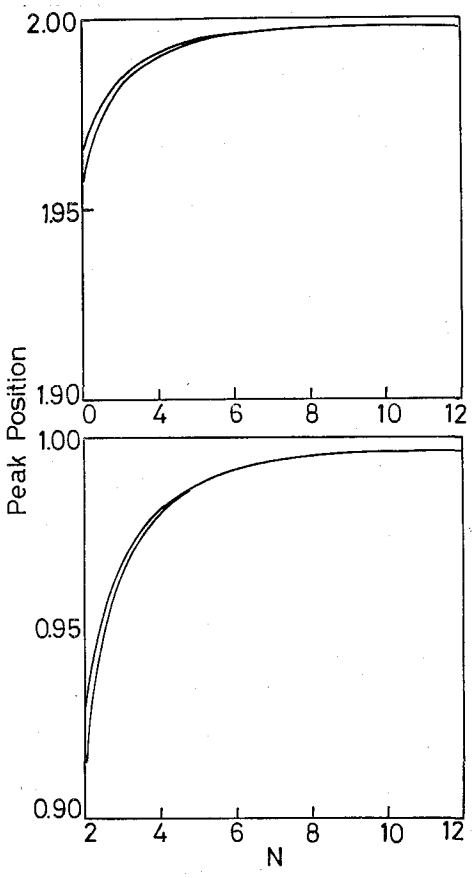

Fig. 3 Peak postion *vs.* number of coherent lamellae N for the first and second order reflections.

as a function of α for various values of N are shown in Fig. 2. The peak position is almost independent of α except for $N=2$, but depends on the number of N. Therefore, the peak positions are replotted as a function of N in Fig. 3 ; lower and upper curves show the limits between which the peak position fluctuates dependent on α. As is seen from the figure, the effect of N is considerably large for $N \leqq 8$ and becomes negligibly small for $N>8$. In the case of no lattice fluctuation within the cluster as in this study, the long spacing calculated from the peak position of the second order reflection is nearer to the true value than that from the first order reflection since the slope of the structure factor is much greater at $\xi=1.0$ than at $\xi=2.0$. This is seen also from Fig. 3.

In order to explain the difference between long spacings calculated from the first and second order reflections reported by Reinhold *et al.*,[1] it has been assumed that the number N of coherent lamellae decreases with increasing annealing time t since the increase of long spacing is mainly caused by the selective melting of unstable thinner

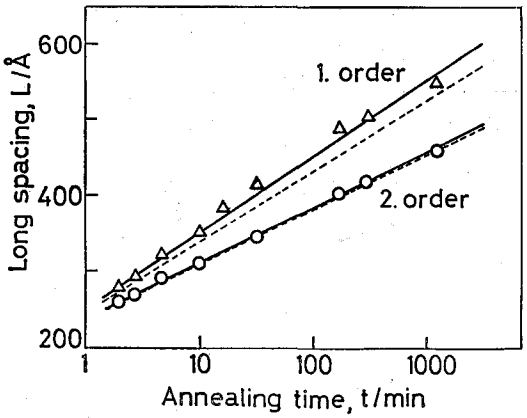

Fig. 4 Annealing time(t) dependence of long spacing(L) of bulk polyethylene calculated from the first and second order reflections when annealed at 130°C. Data from Reinhold, Fischer and Peterlin.[1] Broken lines designate the values corrected for the cluster size.

single lamellae and subsequent slight thickening of thicker lamellae. The results of Fischer *et al.*[1] were examined using the curves in Fig. 3 by assuming that the initial average number of coherent lamellae in the sample is six. The results are shown with broken lines in Fig. 4. In the case of the first order reflection the long spacing corrected for the cluster size becomes by 4.4 % smaller than the observed value, whereas in the case of the second order reflection it hardly changes. Thus, 25 % of the difference between long spacings calculated from the first and second order reflections is elucidated. The residual difference may be due to the second kind of disorder in the lattice function ; the effect of such distance fluctuation will be reported elsewhere.

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